



August 9, 2004

Ken Zweibel
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Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period June 09, 2004 to July 09, 2004, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CuInSe₂-based Solar Cells).

Task 2: CuInSe₂-based Solar Cells

In-Line Evaporation

The new 3/8" Se manifold was evaluated with a test matrix of 2 and 4 effusion holes for two different diameters of 3/32" and 3/64". The tests showed that the manifold with two 3/64" holes placed at either side of the Ga source with the Se evaporation temperature at 300°C was acceptable. Under these particular conditions 14 runs were made. The compositional analysis of the CIGS films as obtained by EDS is given in Table 1. The data in Table 1 show acceptable uniformity both run-to-run and within a longer run, i.e. run No.: 70265 where sampling points were 9" apart.

However, by the end of this series of experiments it was found that, because of its porosity, graphite float keeping the thermocouple on the surface of the liquid Se was soaked with Se. The result of which was that temperature did not represent true surface temperature. Currently the Se source is being redesigned for better controllability and higher capacity.

Table 1. Composition, by EDS, of CIGS films over 14 runs.

Run #	Cu (at%)	In (at%)	Ga (at%)	Se (at%)	Cu / (Ga+In)	Ga / (Ga+In)
70261.12	24.2	17.9	8.7	49.3	0.91	0.33
70262.22	22.0	18.2	8.2	51.6	0.83	0.31
70264.22	24.0	18.5	8.0	49.6	0.91	0.30
<i>70265.12</i>	<i>24.9</i>	<i>18.6</i>	<i>8.4</i>	<i>48.1</i>	<i>0.92</i>	<i>0.31</i>
<i>70265.22</i>	<i>24.4</i>	<i>18.7</i>	<i>7.6</i>	<i>49.3</i>	<i>0.93</i>	<i>0.29</i>
<i>70265.32</i>	<i>23.3</i>	<i>18.8</i>	<i>8.0</i>	<i>50.0</i>	<i>0.87</i>	<i>0.30</i>
<i>70265.42</i>	<i>23.6</i>	<i>18.6</i>	<i>8.4</i>	<i>49.4</i>	<i>0.88</i>	<i>0.31</i>
<i>70265.52</i>	<i>23.2</i>	<i>18.6</i>	<i>7.9</i>	<i>50.2</i>	<i>0.87</i>	<i>0.30</i>
<i>70265.62</i>	<i>22.9</i>	<i>18.2</i>	<i>9.1</i>	<i>49.9</i>	<i>0.84</i>	<i>0.33</i>
<i>70265.72</i>	<i>24.4</i>	<i>15.9</i>	<i>10.4</i>	<i>49.4</i>	<i>0.93</i>	<i>0.39</i>
<i>Average</i>	<i>23.8</i>	<i>18.2</i>	<i>8.5</i>	<i>49.5</i>	<i>0.89</i>	<i>0.32</i>
<i>Std Dev</i>	<i>0.8</i>	<i>1.0</i>	<i>0.9</i>	<i>0.7</i>	<i>0.04</i>	<i>0.04</i>
70268.12	22.3	20.0	7.3	50.4	0.82	0.27
70268.32	22.1	19.6	7.9	50.4	0.80	0.29
70269.22	21.5	19.5	6.9	52.1	0.81	0.26
70270.22	24.0	17.9	7.9	50.2	0.93	0.31
70271.22	24.0	18.7	7.7	49.7	0.91	0.29
70272.12	21.6	19.9	7.6	50.9	0.79	0.28
70272.22	23.2	19.4	7.7	49.7	0.86	0.28
70275.22	23.6	17.8	8.1	50.6	0.91	0.31
70276.22	24.0	17.8	8.1	50.2	0.93	0.31
70277.22	23.6	18.3	7.6	50.5	0.91	0.29
70278.22	24.7	18.1	7.7	49.5	0.96	0.30
70279.22	24.4	18.3	8.3	49.1	0.92	0.31
<i>Average</i>	<i>23.3</i>	<i>18.6</i>	<i>7.9</i>	<i>50.2</i>	<i>0.88</i>	<i>0.30</i>
<i>Std Dev</i>	<i>1.1</i>	<i>0.8</i>	<i>0.4</i>	<i>0.8</i>	<i>0.05</i>	<i>0.02</i>

The new Cu source boat which has been in operation for more than 6 months has shown to be highly reliable and robust. Consequently, the Ga and In sources will be switched to the same boat design.

Fundamental Materials and Interface Characterization

Emitter Layer Deposition and Junction Characterization

The Cu(InGa)Se₂/emitter layer interface is being characterized with a particular objective to optimize the high-utilization chemical surface deposition (CSD) of CdS [1] for Cu(InGa)Se₂ devices. Previously, the device efficiency with CSD was found to be slightly lower than with baseline CBD CdS. We proposed that the difference may be due to etching or other chemical treatment of the Cu(InGa)Se₂ surface which occurs in the first stage of CBD growth. In the CBD process, the films are inserted into the bath containing thiourea and ammonium hydroxide for 1 minute prior to addition of CdSO₄ which initiates the reaction to form CdS. Evidence of a surface etch from the ammonia is provided by optical characterization of a Cu(InGa)Se₂ film which has been oxidized by exposure to humid air in the laboratory. In this case, the optical parameters measured by spectroscopic ellipsometry cannot be fit with a standard optical model [2]. After a 1 minute etch in 28 ml of 30% NH₄OH diluted in 150 ml H₂O, identical to the concentrations in the CBD process, the measurements fit the optical model developed for peeled Cu(InGa)Se₂ with minimal exposure to air. This suggests that the ammonia etches an oxide layer on the Cu(InGa)Se₂. In the CSD process, the solutions including the CdSO₄ are applied directly to the hot Cu(InGa)Se₂ surface and the reaction begins immediately.

Cu(InGa)Se₂ from 2 different runs, with Ga/(In+Ga) \approx 0.25, had CdS deposited by baseline CBD, and CSD deposited in 2 coats at 65°C both with and without a pre-etch in ammonia solution as described above. During the CSD process it was observed that the wetting of the etched Cu(InGa)Se₂ was different than the un-etched films. Specifically, a low contact angle was observed on the un-etched Cu(InGa)Se₂ suggesting a higher surface energy. With the NH₃-etched Cu(InGa)Se₂ a high contact angle was observed similar to deposition glass, suggesting lower surface energy.

The results for the best cell on each piece are summarized in Table 2 and the uniformity among 6 cells on each piece was good. In each case, the efficiency with CSD CdS, with or without the pre-etch, is comparable within statistical uncertainty, to the CBD samples. However, the V_{OC} is \sim 30 mV lower with the CSD process. JV and QE curves show no qualitative differences in behavior but more detailed J-V analysis is being completed. In addition, some of the samples were given a 2 min air heat treatment at 200°C but there was no significant difference.

While the difference in V_{OC} is small it has been observed reproducibly in several experiments and shows that the CdS deposition process has a complicated effect on device performance. Further experiments will evaluate other surface Cu(InGa)Se₂ treatments prior to CSD deposition to help understand the relationship between the surface chemistry and electronic properties.

Table 2. Effects of NH₃ etching Cu(InGa)Se₂ prior to CSD CdS.

CdS Process	Sample #	condition	η (%)	V _{OC} (Volts)	J _{SC} (mA/cm ²)	FF (%)	R _{OC} (Ω -cm ²)	G _{SC} (mS/cm ²)
CBD control	33846.23	as-dep	12.7	0.616	28.6	72.2	1.8	3
	33847.23	as-dep	12.9	0.605	29.2	73.1	1.8	2
	33847.23	HT*	13.6	0.609	30.3	73.5	1.6	0
CSD	33846.12	as-dep	12.3	0.584	30.4	69.4	2.0	2
	33847.12	as-dep	11.9	0.580	28.7	71.6	1.9	3
	33847.12	HT*	12.4	0.575	29.9	72.0	1.8	2
NH ₃ / CSD	33846.13	as-dep	12.6	0.582	30.0	72.5	1.8	4
	33847.13	as-dep	12.3	0.584	28.3	74.4	1.7	0
	33847.13	HT*	12.9	0.571	30.9	73.1	1.7	3

HT* - heat treated for 2 min at 200°C in air.

Mo/CuInSe₂ Interface Characterization

Characterization of the Mo/CuInSe₂-alloy interface is continuing in an attempt to determine the fundamental characteristics that control adhesion and affect device performance. We have previously reported characterization of the orientation of the MoSe₂ layer formed by reaction of Mo, Mo/Ga, and Mo/Cu layers in elemental Se at 450°C for 60 min. Further experiments have been undertaken to characterize the MoSe₂ growth after deposition and peeling of CuInSe₂-alloy films and compare CuInSe₂, Cu(InGa)Se₂, and Cu(InAl)Se₂ films. The Cu(InAl)Se₂ films in particular have poor adhesion with increasing Al content. A number of films were peeled from the substrate and XRD scans measured using a Cr tube for higher resolution. However, it was found that they were not reproducible and changed with time. This has been attributed to the reaction of the MoSe₂ with the oxygen, and probably H₂O, present in the atmosphere. Procedures have been modified to minimize surface oxidation and experiments are being repeated.

Wide Bandgap Solar Cells

Evaporated Cu(InGa)Se₂

The effect of the Cu(InGa)Se₂/emitter layer interface and band alignment on wider bandgap devices is being studied by changing the alloy compositions of the Cu(InGa)Se₂ layers and comparing CdS and Cd_{1-x}Zn_xS emitter layers. For this purpose, Cd_{1-x}Zn_xS layers were deposited by CBD and CSD processes.

QE measurements are very useful to characterize the thickness and bandgap of the Cd_{1-x}Zn_xS layers. The blue response in the QE curves for 4 samples from a single

Cu(InGa)Se₂ run are shown in Figure 1. The curves shown were measured at OV under white light bias and were all normalized to 1 at the maximum response which occurs at ~ 550 nm. E_g was determined from the wavelength shift at $QE_{norm} \approx 0.9$. It is assumed that the CdS has $E_g = 2.42$ eV. Then Figure 1 shows an E_g shift of 0.1 ± 0.03 eV so both the CBD and CSD Cd_{1-x}Zn_xS films have $E_g = 2.52$ eV. For the Cd_{1-x}Zn_xS, this corresponds to a composition with $x = 0.12$ using a bowing parameter of 0.6. The target bandgap was 2.6 eV and the Zn concentration will be adjusted in future experiments.

The CdS and (CdZn)S thicknesses were determined from the value of normalized QE at $\lambda = 400$ nm assuming that the loss in the normalized QE is due exclusively to CdS absorption and no light absorbed in the emitter layer is collected. Then:

This calculation used $\alpha = 1.45 \times 10^5 \text{ cm}^{-1}$ for the CdS and $1.34 \times 10^5 \text{ cm}^{-1}$ for the Cd_{1-x}Zn_xS. Results are listed in Table 3. The thicknesses for the CDS layers agree very closely to the those on annealed ITO control substrates.

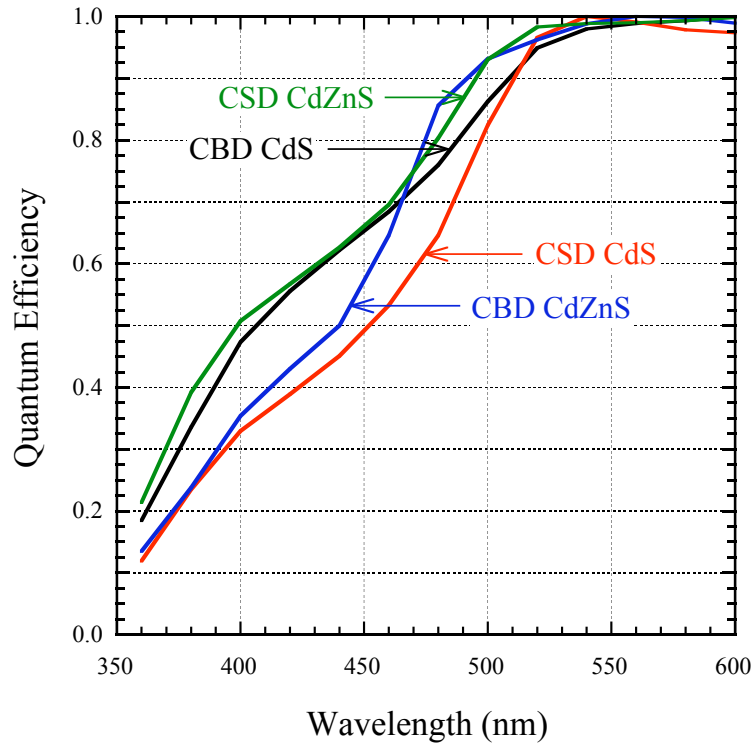


Figure 1. Normalized short wavelength QE used to determine thickness and E_g of CdS and Cd_{1-x}Zn_xS emitter layers deposited on Cu(InGa)Se₂.

Table 3. Thicknesses (d) of CdS and Cd_{1-x}Zn_xS determined from the normalized QE.

emitter layer	QE _{norm} (400nm)	d(CdS)	d(Cd _{1-x} Zn _x S)
CBD CdS	0.47	52	—
CBD Cd _{1-x} Zn _x S	0.35	—	78
CSD CdS	0.33	76	—
CSD Cd _{1-x} Zn _x S	0.51	—	50

Device results comparing narrow 1.2 eV [Ga/(In+Ga) \approx 0.3] and wide 1.5 eV [Ga/(In+Ga) \approx 0.75] bandgap absorber layers with CdS and Cd_{1-x}Zn_xS emitter layers deposited by CBD and CSD are summarized in Table 4 for the best cell with each case. All results are after a 2 min air heat treat at 200°C which resulted in an increased Voc and η for the wider bandgap cells with little difference for the 1.2 eV cells. The different emitter layers generally gave comparable J_{SC} and FF but the CBD CdS always resulted in the highest V_{OC}. With the wider bandgap in particular, it has been proposed that the interface band alignment might limit V_{OC} and raising the emitter layer conduction band could the improve V_{OC}. These experiments, however, do not support this.

Table 4. Solar cell parameters for Cu(InGa)Se₂ with Eg = 1.2 or 1.5 eV with CdS and (CdZn)S emitter layers deposited by CBD or CSD.

Cu(InGa)Se ₂	Sample #	CdS type	η (%)	Voc (Volts)	Jsc (mA/cm ²)	FF (%)
1.2 eV	33847.23	CBD CdS	13.6	0.609	30.3	73.5
	33847.12	CSD CdS	12.4	0.575	29.9	72.0
	33847.32	CBD CdZnS	11.9	0.557	30.0	71.1
	33847.31	CSD CdZnS	10.8	0.558	27.7	70.1
1.5 eV	33857.23	CBD CdS	9.2	0.782	18.3	64.4
	33857.12	CSD CdS	8.8	0.700	18.3	68.4
	33857.32	CBD CdZnS	7.1	0.595	18.4	65.1
	33857.31	CSD CdZnS	7.5	0.641	18.1	64.5

Cu(InGa)(SeS)₂ Selenization

Cu/Ga/In layers will be reacted in H₂Se and/or H₂S to determine the effect of the time-temperature-concentration profiles in controlling the Cu(InGa)(SeS)₂ through-film composition profiles. Sequentially sputtered Cu/Ga/In precursor layers were deposited and found to contain “spits” that were identified as Ga-rich. The Ga sputter target, fabricated in-house by melting high purity Ga metal into a hollowed Cu plate, was found to be contaminated. Consequently, a new Ga target has been fabricated so calibrations of

the precursor layers could be completed. The H₂Se/H₂S reactor was also upgraded with a new turbo pump and H₂Se cylinder.

Sincerely,

Robert W. Birkmire Director

RWB/bj

cc: Gerri Hobbs, UD Research Office
Carolyn Lopez, NREL
Paula Newton
Erten Eser
William N. Shafarman

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1. B. E. McCandless and W. N. Shafarman, *Proc. 3rd World Conf. Photovoltaic Energy Conversion* (2003).
 2. P.D. Paulson, R.W. Birkmire. and W.N. Shafarman, *J. Appl. Phys.* **94**, 879-88 (2003).